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KINETICS OF METAL ATOM OXIDATION
REACTIONS

Arthur Fontijn, et al

Aero-Chem Research Laboratories, Incorporated

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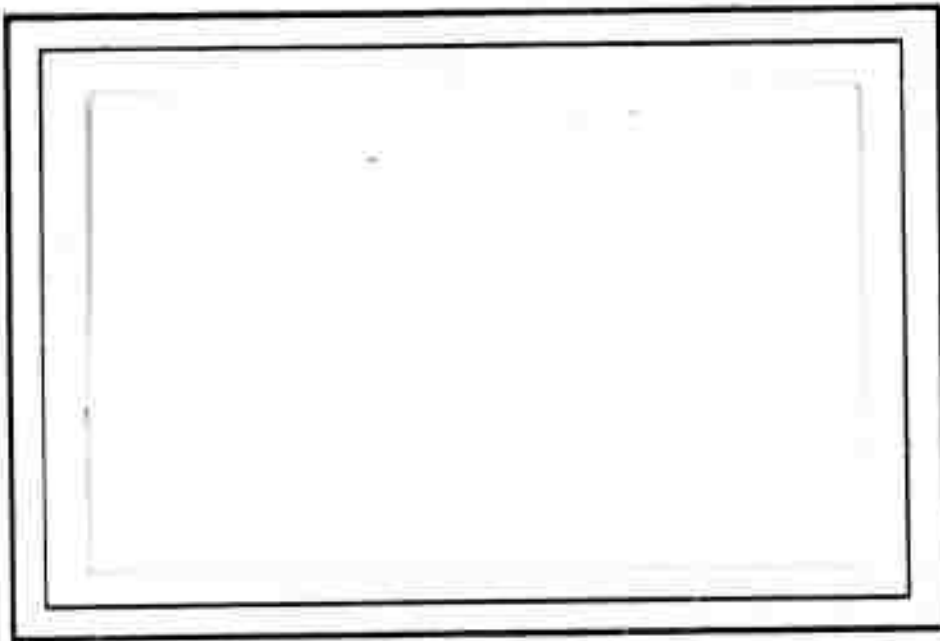
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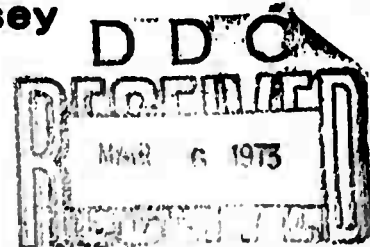


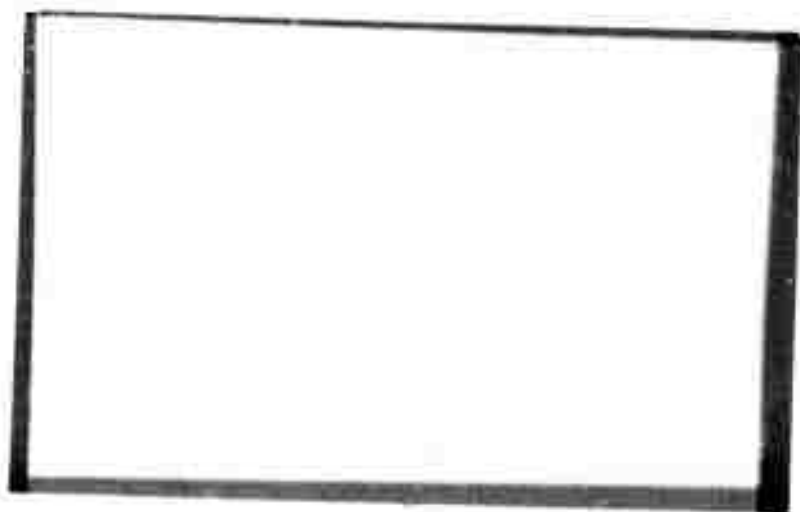
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KINETICS OF METAL ATOM OXIDATION
REACTIONS

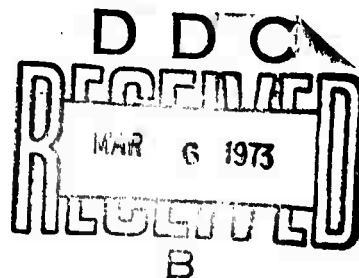
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Arthur Fontijn, William Felder
and James J. Houghton

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13. ABSTRACT

For predictions regarding observables in nuclear fireballs and their effect on defense discrimination capabilities, the rates of oxidation of several free metal atom species need to be known. The goal of the present work is to measure the rate coefficients (and their temperature dependence) for the reactions of gaseous Al and Fe with O₂ and O₃. The apparatus used is a cylindrical fast-flow reactor, suitable for the study of the reaction kinetics of various gaseous species at temperatures up to ~2000 K. In these studies, metal is vaporized and entrained in an inert carrier gas stream. O₂ is introduced into this gas stream at concentrations much larger than that of the metal atoms. Rate coefficients are obtained from the observed variations in the relative metal atom concentrations (measured in absorption) as a function of reaction time, O₂ concentration, total pressure, and temperature.

Measurements of the kinetics of the homogeneous gas phase reaction between Al and O₂ at 1400 K have been completed. The reaction proceeds via $\text{Al} + \text{O}_2 \xrightarrow{k_1} \text{AlO} + \text{O}$ with a rate coefficient of $(4.1 \pm 2.0) \times 10^{-11} \text{ ml molecule}^{-1} \text{ sec}^{-1}$.

To determine the temperature dependence of k_1 over the temperature range of interest to ARPA/DNA and to study the kinetics of the reactions of Al and Fe with O₃, temperatures much lower than 1400 K are required. To this end, we have now modified the apparatus to allow measurements of small metal atom concentrations based on the more sensitive fluorescence technique rather than on the absorption technique. Our first experiments indicate that by working in this mode the rate coefficients of Al reactions can be measured down to at least 300 K. This obviates the need for constructing the wall-less reactor previously considered for these measurements.

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SUMMARY

For predictions regarding observables in nuclear fireballs and their effect on defense discrimination capabilities, the rates of oxidation of several free metal atom species need to be known. The goal of the present work is to measure the rate coefficients (and their temperature dependence) for the reactions of gaseous Al and Fe with O_2 and O_3 . The apparatus used is a cylindrical fast-flow reactor, suitable for the study of the reaction kinetics of various gaseous species at temperatures up to ≈ 2000 K. In these studies, metal is vaporized and entrained in an inert carrier gas stream. O_2 is introduced into this gas stream at concentrations much larger than that of the metal atoms. Rate coefficients are obtained from the observed variations in the relative metal atom concentrations (measured in absorption) as a function of reaction time, O_2 concentration, total pressure, and temperature.

Measurements of the kinetics of the homogeneous gas phase reaction between Al and O_2 at 1400 K have been completed. The reaction proceeds via $Al + O_2 \xrightarrow{1} AlO + O$ with a rate coefficient of $(4.1 \pm 2.0) \times 10^{-11}$ ml molecule $^{-1}$ sec $^{-1}$.

To determine the temperature dependence of k_1 over the temperature range of interest to ARPA/DNA and to study the kinetics of the reactions of Al and Fe with O_3 , temperatures much lower than 1400 K are required. To this end, we have now modified the apparatus to allow measurements of small metal atom concentrations based on the more sensitive fluorescence technique rather than on the absorption technique. Our first experiments indicate that by working in this mode the rate coefficients of Al reactions can be measured down to at least 300 K. This obviates the need for constructing the wall-less reactor previously considered for these measurements.

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I. INTRODUCTION

The goal of the present work is to measure rate coefficients for the reactions of gaseous Al and Fe with O_2 and O_3 required for various Department of Defense applications.

The measurements are made with a cylindrical fast flow reactor apparatus suitable for study of the reaction kinetics of various gaseous species at temperatures up to ≈ 2000 K. Rate coefficients are obtained from the observed variations in the relative metal atom concentrations as a function of reaction time, O_2 concentration, and total pressure. The flow reactor is a high purity alumina cylindrical tube situated inside a vacuum furnace.^{1,2} The reactor and vacuum jacket have ports for optical observations. In these studies metal is vaporized and entrained in an inert carrier gas stream. The O_2 is introduced into this gas stream at concentrations much larger than that of the metal atoms. The basic measurement of the relative metal atom concentration as a function of reaction time has thus far been made via optical absorption of the requisite metal atom radiation emitted by a hollow-cathode lamp.[†] To span a wider temperature range than is possible using absorption, apparatus modifications have been made to permit the much smaller metal atom concentrations obtained near 300 K to be measured by resonance fluorescence.

Under this contract, we have measured the rate coefficient of the reaction



at 1400 K. Details of these measurements, made in the absorption mode, are reported in Section II.

Our next task is to determine the temperature dependence of Reaction (1) and of the reaction



which we previously studied at 1600 K.¹ This requires operation at much lower temperatures, preferably as low as 300 K. Temperatures at least as low as 500 K are necessary to allow measurements of the Al and Fe reactions with O_3 ,

[†] $[Me]_{rel} = [Me]/[Me]_i = \ln(I_0/I)/\ln(I_0/I)_i$ in which the i denotes initial conditions, and I_0 the transmitted light intensity in the absence of metal atoms.

another task of the present work. To be able to work at these temperatures we had originally considered using a wall-less reactor.³ Further studies suggest that resonance fluorescence measurements in the present apparatus in a modified form would be a more convenient method. Successful preliminary experiments in the fluorescence mode have already been performed which indicate that reaction temperatures at least as low as 300 K can be used. This work is discussed in Section III.

II. Al/O₂ KINETICS AT 1400 K

A. Experimental

The method of obtaining and reducing the data is the same as for the Fe/O₂ experiments.^{1,4} We again used two absorption lines of different oscillator strengths (309.3 nm, $gf = 0.73$ and 394.4 nm, $gf = 0.23$)⁵ to prevent any systematic errors due to the specific Al concentrations used or deviations from the Lambert-Beer law.

Al was supplied from a 4 cm deep, wide-lipped boron nitride crucible. The crucible was first preheated to ≈ 1100 K under vacuum in a bell jar, brought up to 1 atm pressure with Ar and filled with high purity Al wire (or shot). The Ar pressure was then slowly reduced to 1 Torr, and the crucible kept hot until the molten Al stopped bubbling. After cooling, the crucible was placed inside an alumina sleeve and inserted through a vacuum feedthrough into the most upstream of the three separately heated contiguous reactor sections. To provide an adequate Al flow, the section containing the Al source was kept at 1600 to 1700 K, 200 to 300 K higher than the reaction zone temperature.

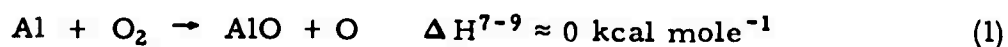
Typically, Ar was used as the bath gas. In one series of runs in which N₂ bath gas was used instead, the results were consistent with the Ar work. However, as noted before¹ at 1700 K, the N₂ data showed more scatter. Additionally, qualitative evidence was obtained for a slow reaction (heterogeneous or homogeneous) between Al and N₂.

The reaction conditions used are shown in Table I (page 4). [Al] may be estimated from optical absorption measurements following a method used by Linevsky.⁶ The fractional absorption in our experiments varied at both wavelengths used from as high as $\approx 90\%$ with no oxidizer present to $\approx 1\%$ at the detection threshold. These limits can be translated into densities of approximately $5 \times 10^{12} > [\text{Al}] > 2 \times 10^{10} \text{ ml}^{-1}$ at 394.4 nm and $9 \times 10^{11} > [\text{Al}] > 4 \times 10^9 \text{ ml}^{-1}$ at 309.3 nm. For the experiments reported here, $1 \times 10^{13} < [\text{O}_2] < 2 \times 10^{14} \text{ ml}^{-1}$. The data reduction method used^{1,4} assumes $[\text{O}_2] \gg [\text{Me}]$.

Although not strictly fulfilled over the entire range of Al and O₂ concentrations, this conditions is adequately satisfied over the useful range of running conditions as indicated by the linearity of plots such as Fig. 1 and by the internal consistency of the data.

B. Results and Discussion

Figure 1 shows a typical first order data plot. The pseudo-first order rate constants, k_{ps1} , obtained from such runs are plotted against [O₂], as in Fig. 2, to yield k_1 , the second-order rate coefficient. The values of k_1 obtained from such series of runs are listed in Table I. They are seen to be independent of [M], demonstrating that the predominant Al oxidation path is bimolecular, i. e. the reaction is



The measured values of k_1 are apparently[†] also independent of \bar{v} , the average gas velocity and of the absorption lines used, indicating that the data are free of systematic errors. The linearity of the observed plots and the relative constancy of the results rule out major influences of other competing processes.

The normalized standard deviation in the determination of k_1 at 1400 K is 40%. Allowing, as in our Fe work,^{1,4} for a possible 20% systematic error and 23% for the uncertainty in η (a parameter used in calculating k_{ps1} from the observed data^{1,4}), the total uncertainty in k_1 is about 50%. Thus, the measured rate coefficient for Reaction (1) is $(4.1 \pm 2.0) \times 10^{-11} \text{ ml molec}^{-1} \text{ sec}^{-1}$ at 1400 K. To our knowledge this measurement constitutes the first experimental determination of this rate coefficient.

[†] The rate coefficient data could be construed as showing a slight trend, increasing with \bar{v} . However, values of k_1 obtained under identical conditions (e. g. 5 Torr, 87 m sec⁻¹; 10 Torr, 118 - 120 m sec⁻¹, see Table I) span the entire range of variation of the measured rate coefficients, indicating that the quality of these data is insufficient to imply such a trend. Further measurements of k_1 at 1400 K will be made as part of the fluorescence studies (below).

TABLE I. RATE COEFFICIENT OF $\text{Al} + \text{O}_2 \rightarrow \text{AlO} + \text{O}$ AT 1400 K

λ (nm)	P (Torr) ^a	v (m sec ⁻¹)	$[\text{O}_2]$ (10^{13} ml ⁻¹)	\bar{T} (K)	k_1 (10^{-11} ml molec ⁻¹ sec ⁻¹)
309.3	5	87	3.3 - 11.1	1417	2.4
309.3	5	87	3.3 - 10.1	1406	5.0
394.4	5	188	2.5 - 9.3	1418	6.0
394.4	6	210	2.3 - 9.1	1400	6.0
309.3	10	40	2.4 - 12.3	1392	3.4 ^b
309.3	10	85	2.2 - 11.4	1400	3.2
309.3	10	184	2.5 - 10.4	1419	6.6
394.4	10	120	1.7 - 9.6	1435	6.6
394.4	10	118	3.3 - 20.5	1411	2.8
309.3	25	85	3.4 - 11.3	1396	4.2
309.3	25	57	6.8 - 17.5	1399	2.2
394.4	25	40	1.2 - 17.4	1411	2.1
309.3	45	79	1.8 - 12.2	1399	3.0
Mean: 1408					4.1

^a 1 Torr = 133.3 Nm^{-2}

^b N_2 bath gas, Ar used as bath gas in all other series

III. RESONANCE FLUORESCENCE MEASUREMENTS

The measured rapid rate of Reaction (1) at 1400 K and its thermo-neutrality suggest that its temperature dependence will be small. In order to measure that temperature dependence accurately, a large range of reaction temperatures must be spanned. In addition, in order to measure the rates of reaction of Al and Fe with O_3 , temperatures below 500 K are necessary because of the rapid thermal decomposition of O_3 at higher temperatures. We previously proposed³ and described a wall-less reactor design in which low temperature (200 to 300 K) Al- or Fe-laden gas flows could be obtained via adiabatic expansion of high temperature gases. As an alternative, we considered the use of resonance fluorescence to be able to work with lower atom concentrations, which in itself, would also allow the use of lower operating temperatures. The success of our first fluorescence experiments is such that there appears at present no need to construct a wall-less reactor.

A. Experimental

To make fluorescence measurements of relative metal atom concentrations an optical path has been provided at right angles to the absorption

path, cf. Fig. 3. This necessitated the use of a 3-hole reactor and heat shields. As the principal heat shields we now use a Zircar[†] blanket held in place by the inner alumina and outer molybdenum heat shield of the original apparatus,^{1,2} cf. Fig. 3.

A hollow-cathode lamp is again used as the light source. For our initial tests of resonance fluorescence we have used the 396.2 nm resonance line of Al and Pyrex optics. The detector is an EMI 9635QB blue-sensitive PMT mounted on a Jarrell-Ash 0.5 m monochromator. The exciting radiation is chopped at 140 Hz and the modulated output of the PMT is detected with a PAR HR-8 lock-in amplifier.

B. Results

Three phases of preliminary testing have been carried out during the last month of this reporting period. The phases comprise: (i) Initial setup, optimization, and feasibility studies of the method at high (1200 -1400 K) temperature, (ii) Determination of the lowest reactor temperature at which Reaction (1) can be studied by resonance fluorescence, and (iii) Optimization of the experimental apparatus for kinetic studies of Reaction (1) at room temperature (currently in progress).

In the initial testing phase, the optical arrangement shown in Fig. 3 replaced the previously uncollimated source, thus reducing scattered light (in phase "noise") by a factor of 20. In addition, blackbody radiation from the heated reactor was found to be a source of "white noise" (noise independent of frequency). A fraction ($\approx 1/1000$) of this noise is included in the bandpass of the tuned amplifier. Lowering the reactor temperature from 1400 K to 1200 K reduced the blackbody radiation intensity by a factor of ≈ 3 , and a series of three runs was carried out at 10 Torr pressure. The k_{ps1} derived from these 1200 K runs (see below for data treatment) were consistent with a k_1 on the order of 10^{-10} ml molec⁻¹ sec⁻¹, comparable to that measured at 1400 K (Section II).

For the second phase of testing, we resistively heated the Al containing crucibles and controlled the reactor temperature independently. As expected, a drop from 1200 to 800 K reduced the blackbody radiation to negligible levels. The object of these experiments was to find the lowest temperature at which Al vapor could be seen in fluorescence. That temperature has

[†] Zircar blanket is a new zirconium oxide product from Union Carbide. It is flexible, can be cut with scissors, and its use considerably facilitates the construction and reduces the power consumption of vacuum furnaces such as ours.

been found to be 300 K, and is apparently limited only by the fact that the reactor cannot be cooled in its present form.

The current phase of testing is aimed at producing a stable, workable concentration of Al for experiments to be made at room temperature. Obtaining useful Al concentrations (fluorescence $S/N > 10$) at this temperature has been found to be straightforward. However, stability of signal level and reactor temperature is more difficult to maintain because (i) the external crucible heating coil is subject to burnouts due to overheating and to electrical shorts due to molten Al overflow from the crucible and (ii) heat transfer from the hot crucible to the bath gas is sufficient to cause a slow, steady rise in the reactor temperature. We have attacked these problems by (i) using smaller (≈ 1 cm deep) crucibles insulated with Zircar blanket (ii) placing the crucible below (≈ 1 cm) the main bath gas inlet and dividing the bath gas flow so that from 10-25% enters below the crucible to entrain Al vapor. These two steps reduced heat transfer to the bath gas sufficiently to allow the reactor temperature to be maintained at ≈ 300 K. The problems associated with the external heater are also lessened, but require further work. Some redesigning of the source section of the apparatus is needed.

C. Discussion

1. Data Handling

As in our absorption experiments^{1,4} we need only be concerned with relative metal atom densities in order to extract k_1 from the data. Under optically thin conditions (no re-absorption of the emitted photons) and when the radiation rate of the fluorescing state is much greater than its quenching rate, the fluorescence signal, F , is given by

$$F = GI\sigma l [Me] \quad (A)$$

where I is the lamp intensity, σ is the resonance absorption cross section, l is the length of the fluorescing region, and G is a constant instrumental factor which includes the solid angle subtended by the detector, photo-multiplier tube (PMT) sensitivity, etc. From Eq. (A)

$$[Me]_{rel} \equiv \frac{[Me]}{[Me]_i} = F/F_i \quad (B)$$

where $[Me]_i$ and F_i are the initial metal atom density and fluorescence signal. Then, $a \equiv -d \ln[Me]/dx$ is obtained from the local slope of a plot of $\ln F/F_i$ versus x , the distance from the oxidizer inlet to the observation window, cf. Fig. 4. Using this value of a , the analysis proceeds as before^{1,4} to determine k_{ps1} and hence k_1 .

2. Criteria of Validity and Detection Limits

Equation (A) is valid under optically thin conditions with no quenching, but Eq. (B) is valid under optically thin conditions provided only that quenching is constant. The constant quenching condition is fulfilled here, as can be seen from the following argument. The only change in species present during an experiment is from Al to AlO and from O₂ to O. [AlO] and [O] are present to $\approx 10^{12}$ ml⁻¹ and, even assuming a large quenching rate coefficient of 10^{-10} ml molec⁻¹ sec⁻¹, they can affect k_{ps1} by less than 10^2 sec⁻¹, which is less than 10% of k_{ps1} . The range of optically thin conditions can be determined by making a normalized plot of fluorescence intensity versus [Al]. At low [Al], the plot is linear with unit slope. At higher densities it deviates due to re-absorption. The linear region is the optically thin range of [Al]. For the 396.2 nm line, [Al]_{max} for optically thin conditions was found to be $\approx 10^{11}$ ml⁻¹ (30% absorption), cf. Fig. 5.

The noise sources listed above are, in principle, the only limits of practical significance in the present system. A new quartz optical system, to be installed shortly, should aid in reducing them and enhancing the signal. The new lens system will yield a parallel focused beam of 0.6 cm diam thus reducing scattered light. It will also gather more light from the hollow cathode source than the present arrangement thereby increasing the signal. Finally, quartz optics will allow us to use uv resonance lines of Al (e.g. 309.3 nm) hence reducing background unmodulated interferences. We estimate that the overall improvement in S/N will be by at least a factor of 10 from the present system. Such an improvement is of major importance to our 300 K work where the achievable Al concentrations[†] are lower than at 1200 K.

3. Comparison with the Planned Wall-less Reactor

The tests described above indicate that resonance fluorescence detection is a viable alternative to the wall-less reactor for achieving low temperatures. In addition to requiring no significant down time for building a new apparatus, the resonance fluorescence technique will allow the use of significantly lower values of [Al] than were contemplated for use in the wall-less reactor thus suppressing homogeneous nucleation as a competing loss process for Al while still achieving the desired low temperatures. The results of the preliminary tests also indicate that wall losses in the tubular

[†] No a priori estimate of the absolute detectability limit is possible at present because the factor G in Eq. (A) is not known; however, 2% absorption at 396.2 nm and 1200 K ([Al] $\approx 7 \times 10^9$ ml⁻¹) gave S/N ≈ 100 in fluorescence. This ratio is a factor of 10 greater than necessary for experimental k_{ps1} determinations for which we require a minimum change in signal (atom density) by a factor of 10.

fast flow reactor are less severe than had been anticipated.¹ Thus, the principal advantages of the wall-less reactor are compensated for by the greater sensitivity of resonance fluorescence detection and it appears unnecessary to build a wall-less reactor to complete the program.

IV. PLANS

Our next task is the determination of the temperature dependence of k_1 over the 300-1400 K range using the apparatus in the fluorescence mode. We plan to include measurements at 1400 K, using quartz optics and including the 309.3 nm Al line, to verify the consistency of the measurements by the absorption and fluorescence techniques. We also plan to measure the temperature dependence of k_2 (the Fe/O₂ reaction), previously^{1,4} measured only at 1600 K.

We expect to be able to initiate measurements using O₃ as the oxidizer species. However, completion of rate coefficient measurements for Al/O₃ and Fe/O₃ probably will not be possible within the time and funding limitations of the present contract.

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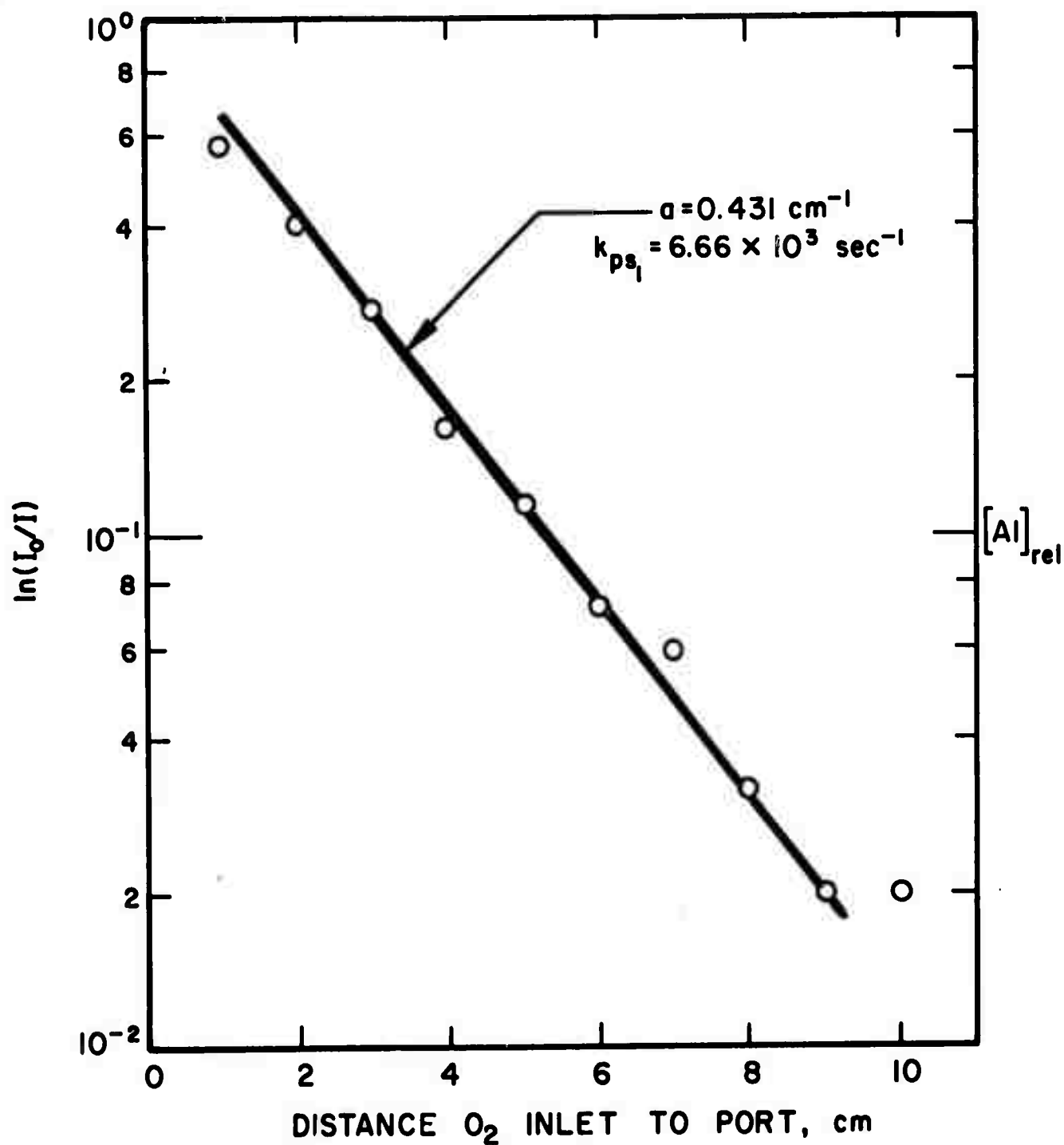


FIG. 1 Al-ATOM CONCENTRATION PROFILE (ABSORPTION)

$\bar{T} = 1413 \text{ K}$
 $\nabla = 118 \text{ m sec}^{-1}$
 $[O_2] = 12.3 \times 10^{13} \text{ ml}^{-1}$
 $\lambda = 394.4 \text{ nm}$
 $P = 10 \text{ Torr}$

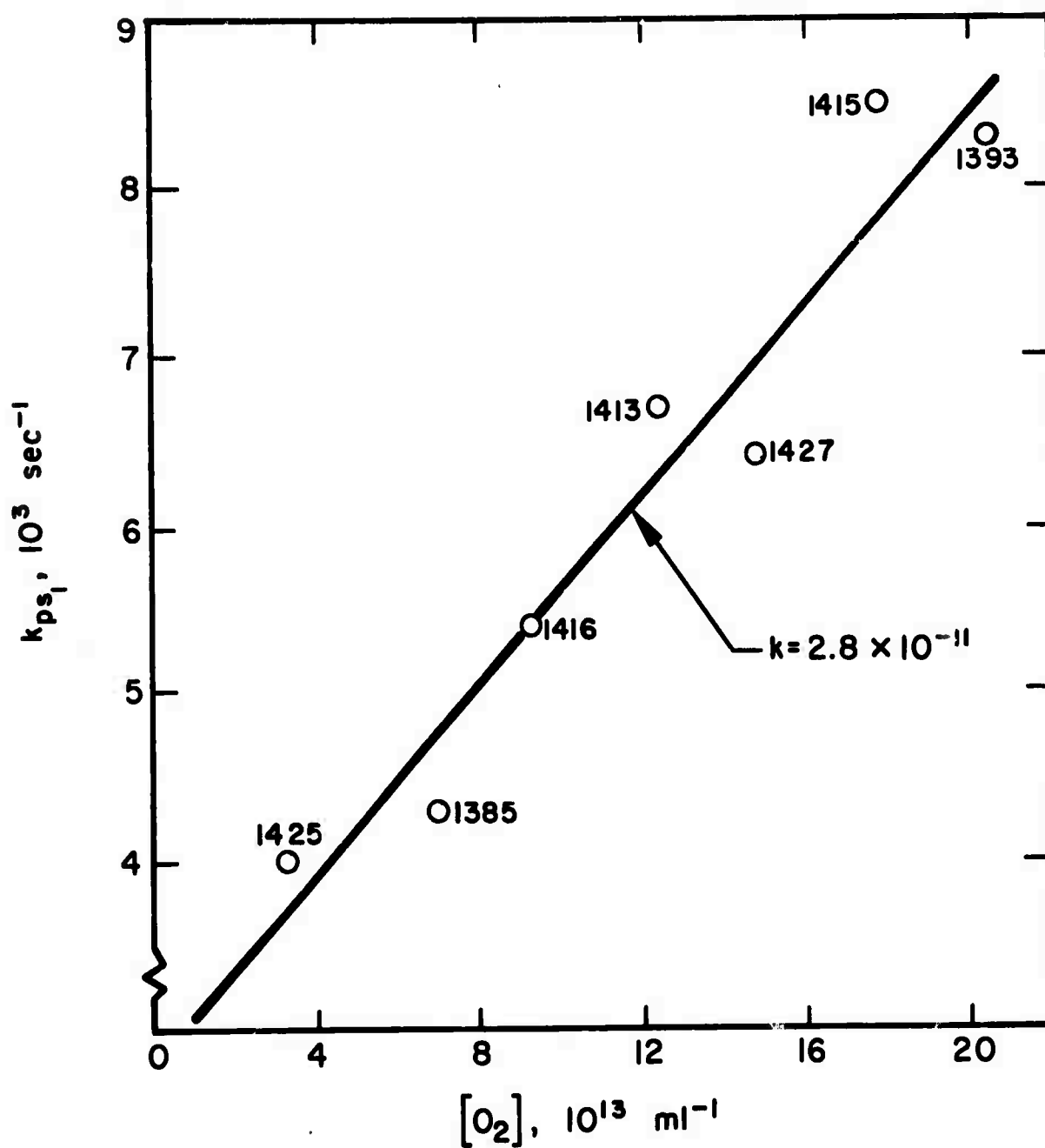


FIG. 2 Al/O₂ RATE COEFFICIENT AT 10 TORR

$$\begin{aligned}\bar{T} &= 1411 \text{ K} \\ \bar{v} &= 118 \text{ m sec}^{-1} \\ [\text{Ar}] &= 6.8 \times 10^{16} \text{ ml}^{-1} \\ \lambda &= 394.4 \text{ nm}\end{aligned}$$

Numbers beside each individual point indicate the \bar{T} at which it was obtained.

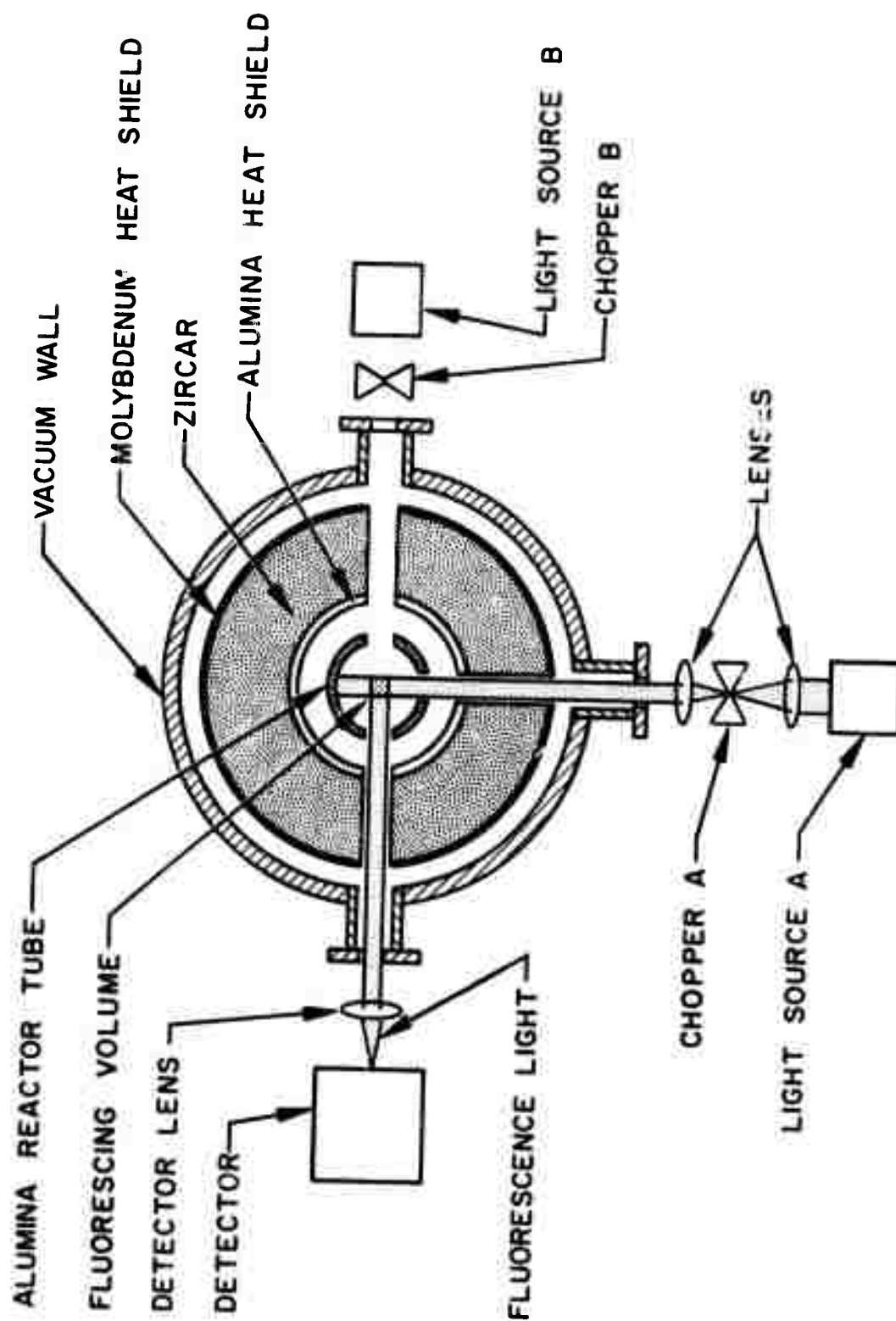


FIG. 3 SCHEMATIC DIAGRAM OF THE EXPERIMENTAL APPARATUS (TOP VIEW)
Source A for fluorescence, Source B for absorption measurements

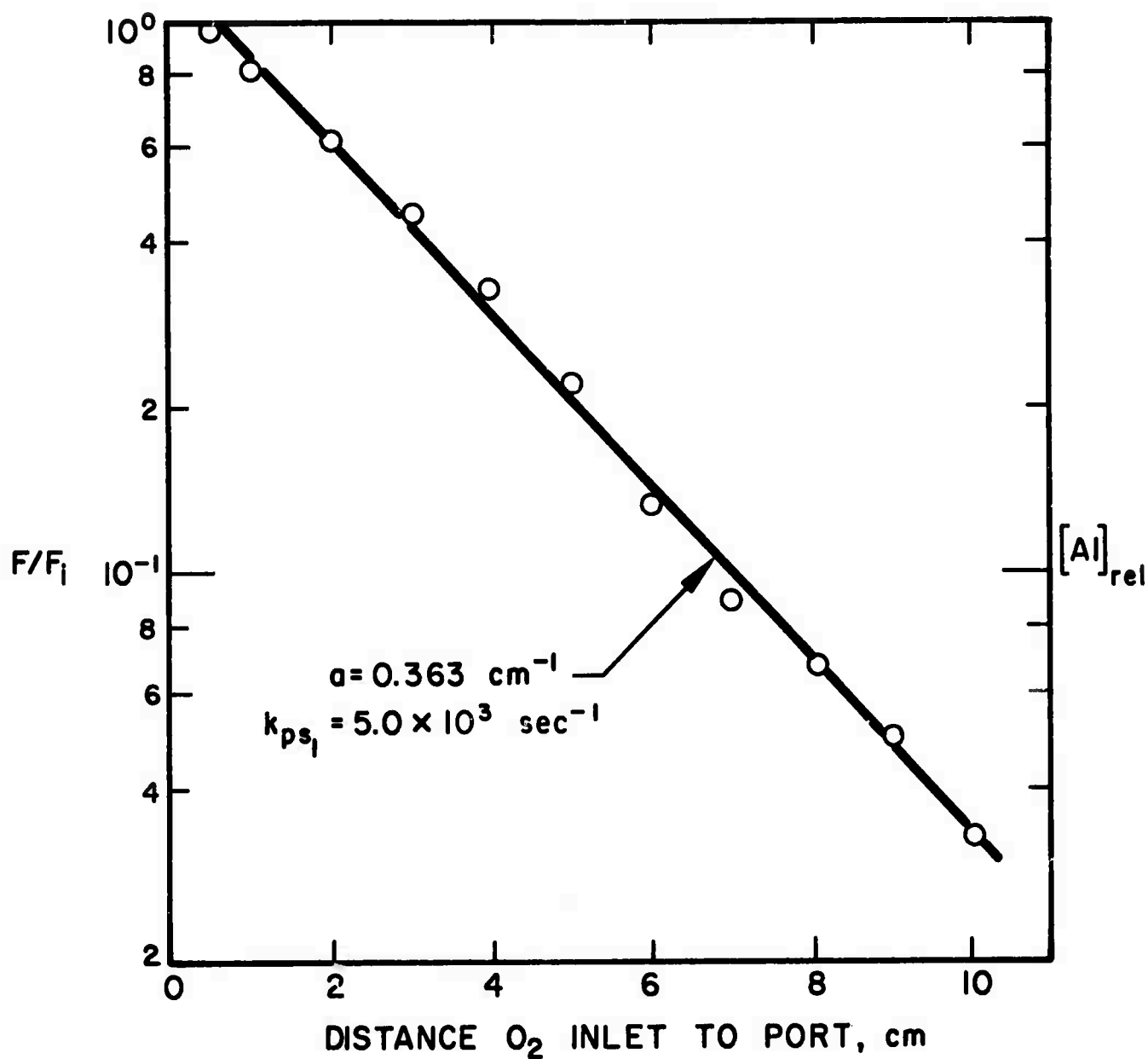


FIG. 4 Al-ATOM CONCENTRATION PROFILE (FLUORESCENCE)

$$\begin{aligned}
 \bar{T} &= 1218 \text{ K} \\
 \bar{v} &= 105 \text{ m sec}^{-1} \\
 [O_2] &= 3.7 \times 10^{13} \text{ ml}^{-1} \\
 \lambda &= 396.2 \text{ nm} \\
 P &= 5 \text{ Torr}
 \end{aligned}$$

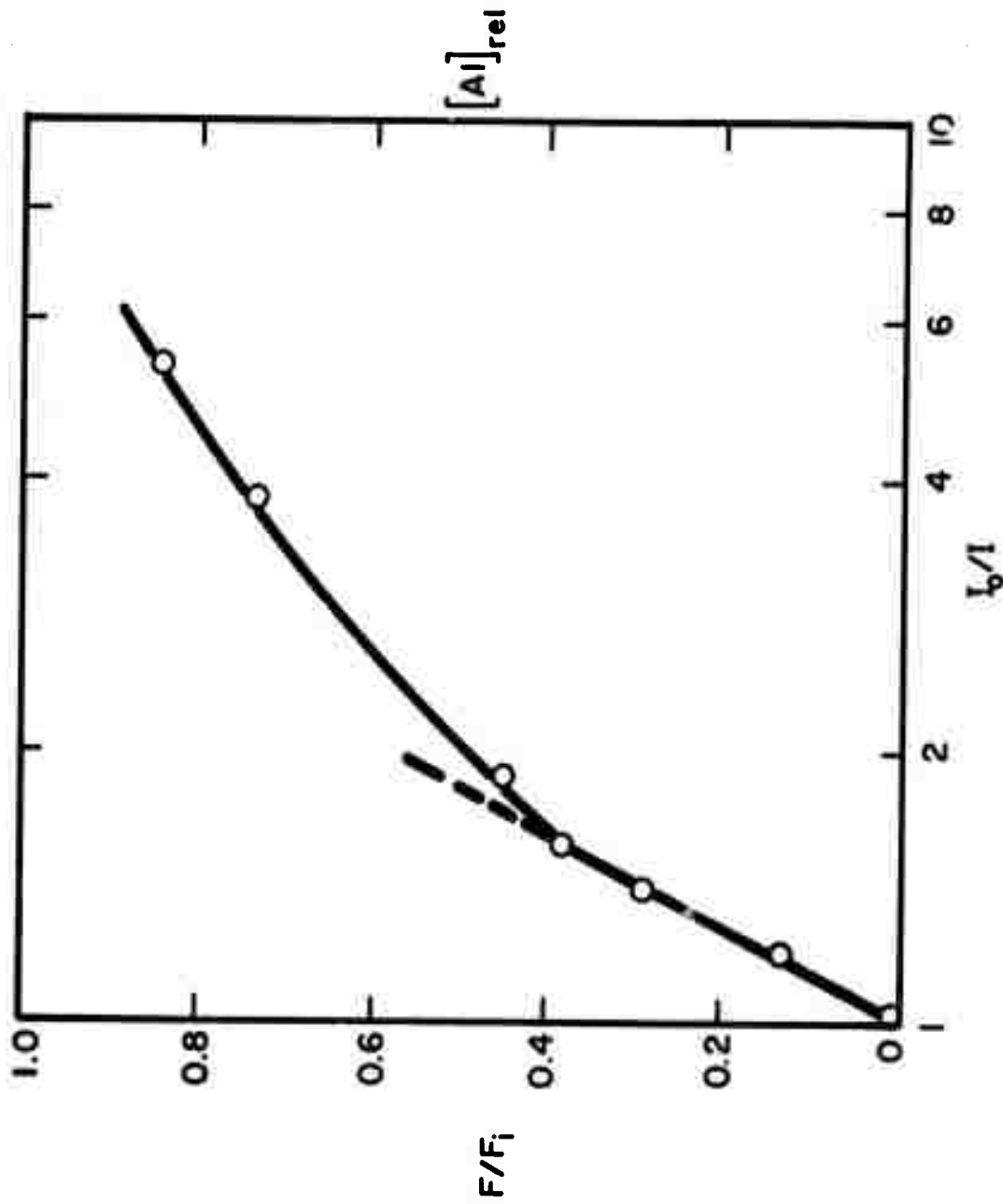


FIG. 5 CURVE OF GROWTH OF Al (396.2 nm) FLUORESCENCE AT 1200 K

The abscissa is the absorption value plotted on a logarithmic scale,
i. e. $\ln(I_0/I) \propto [Al]_{rel}$